Aluminium tri-*iso*-propoxide: Shelf life, transport properties, and decomposition kinetics for the low temperature processing of aluminium oxide-based coatings

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Abstract

Aluminium tri-*iso*-propoxide (ATI) is a common precursor for the MOCVD of alumina coatings. However, little is known on its long term stability while its saturated vapour pressure in function of the temperature is controversial. The present contribution deals with these questions through FTIR, TGA and vapour pressure measurements. Low pressure MOCVD from ATI was performed in the temperature range 250–700 °C. Whereas the pyrolytic decomposition of ATI leads to hydroxo species free alumina films above 415 °C, it is shown in this paper that the thermal decomposition of ATI in the presence of water vapour yields pure alumina films at temperatures as low as 300–350 °C. The films prepared in the range 250–700 °C do not diffract X-rays. Arrhenius plots for both pyrolytic ($E_a \sim 12$ kJ/mole) and water assisted ($E_a \sim 9$ kJ/mole) decomposition reveal diffusion-limited processes with higher growth rate values in the former case.

Keywords: MOCVD; Aluminium tri-iso-propoxide; Amorphous alumina; Thermal analysis; Infra-red spectroscopy; Kinetics

1. Introduction

The MOCVD of aluminium oxides from aluminium tri-*iso*-propoxide (ATI) is well documented, but white spots still remain in the processing-properties relationship and in the mechanisms which control ATI decomposition. These points have been discussed in previous papers [1–4] where we reviewed the MOCVD preparation of alumina thin films and shed some light on the MOCVD from ATI. Reported experiments were performed at low pressure, in the temperature range 350–700 °C, with N_2 as the carrier gas and no additional oxygen sources in the vapour phase (pyrolytic decomposition). Films grown at 350 °C had the formula AlOOH, whereas those grown above 415 °C consisted of amorphous Al_2O_3. Between 350 and 415 °C, partly hydroxylated films were obtained. Some concerns still exist about stability and thermal behaviour of ATI. This paper presents three further developments: i) investigations about ATI aging on exposure to ambient air and upon heating; ii) LP-MOCVD experiments with water vapour added in the gas phase; iii) kinetic data on the growth of alumina films from ATI.

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2. Aluminium tri-iso-propoxide as a MOCVD precursor

2.1. Molecular structure

ATI has a molecular structure made of oligo-nuclear units $[Al(O^iPr)_3]_n$. The degree of association (n) varies with physical state, thermal history and storage conditions [5–11]. The crystal structure consists of tetra-nuclear units $[Al(O^iPr)_3]_4$ [9]. The $Al_4(O_b)_6(O_t)_6$ core is built about a 6-fold coordinated, central Al atom bound to three peripheral Al atoms by three pairs of bridging O_b atoms (Fig. 1). Three pairs of terminal O_t atoms complete the 4-fold coordination of the three peripheral Al atoms. The 'tetrahedral' Al–O bond lengths range from 1.63(2) to 1.78(2) Å and the 'octahedral' ones measure 1.93(1) and 1.94 (1) Å. These bond lengths compare with those measured in the crystal structures of Al_2O_3, AlO(OH) and $Al(OH)_3$. It is therefore not surprising that an oligomer structure persists on vaporization. Mass-spectrometry studies ascertained the presence of oligo-nuclear molecules in the vapour phase. From works by

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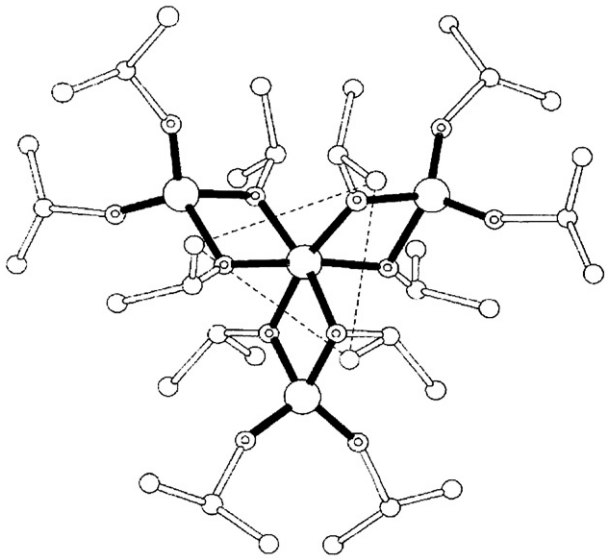

Fig. 1. A view of the tetranuclear structure of ATI emphasizing the Al_4O_{12} core (from Turova et al. [9]).

Fieggen et al. [12], Brown and Mazdiyasni [13] and Daasch and Fales [11], Turova et al. wrote [9]: "*According to mass spectrometric data, gaseous Al(Pr-iso)$_3$ mainly contains trimeric and tetrameric molecules in a ratio depending on the thermal prehistory of the condensed phase*". The trimer–tetramer equilibrium depends on whether the vapour originates from the solid or the melt [8,10]. It should be noted that the tendency of 4-fold coordinated Al atoms to increase their coordination number to 6 may result in further polymerization on long time storage [14].

The oligomer structure of ATI in the vapour phase questions the mechanisms proposed in the literature for its decomposition into Al_2O_3. These mechanisms do not take into account the real structure of ATI. Starting from a supposedly monomer Al(O^iPr)$_3$, they postulate the intermediate formation of molecular $Al(OH)_3$ [15,16] or AlO(OH) [17] in the vapour phase.

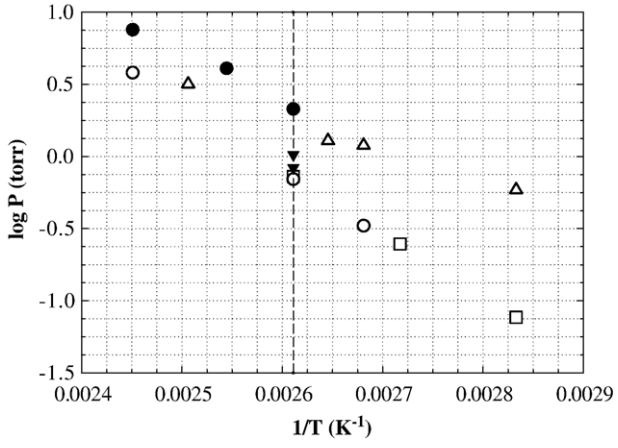

Fig. 2. Clausius–Clapeyron plots of ATI vapour pressure from various studies: open squares [6,17,21–23], dark circles [18], open circles [19], open triangles [20]; dark triangles correspond to the present study.

2.2. Vapour pressure

Several authors have measured ATI vapour pressure against temperature [18–20]. Sladek et Gibert [21] and Morssinkhoff [17] used results from references [6,22]. Aboaf, who pioneered the MOCVD preparation of alumina, reported a value of 667 Pa at 134 °C according to the Belstein [23]. The different studies and the values obtained in the present study (see below) are gathered on the Clausius–Clapeyron plot of Fig. 2. The values found for the vapour pressure at 110 °C (the precursor temperature in our MOCVD experiments) range from 93 to 285 Pa. Our own measurements (static method) yielded values between 120 and 135 Pa at 110 °C (Fig. 2).

The thermal sensitiveness of the molecular structure of ATI, and the ensuing variation of the vapour pressure, may be responsible for dispersed film growth rate values. This leads to recommend using a same charge of ATI for but a very limited number of deposition experiments, in agreement with Cameron [24]: "*The vapour pressure of aluminium isopropoxide is well known to be a complex function of its thermal history. The overall effect of these factors is a gradual decrease in average growth rate over a period of a few weeks. Over a period of a few hours,*

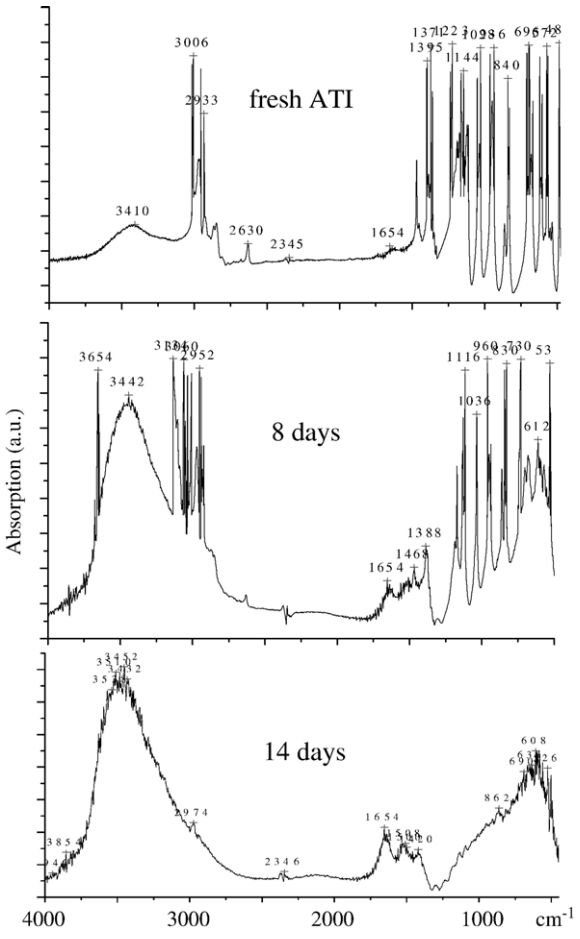

Fig. 3. Absorption FTIR spectra for ATI samples: fresh sample (top), and samples exposed to ambient atmosphere for 8 days (middle) and 2 weeks (bottom).

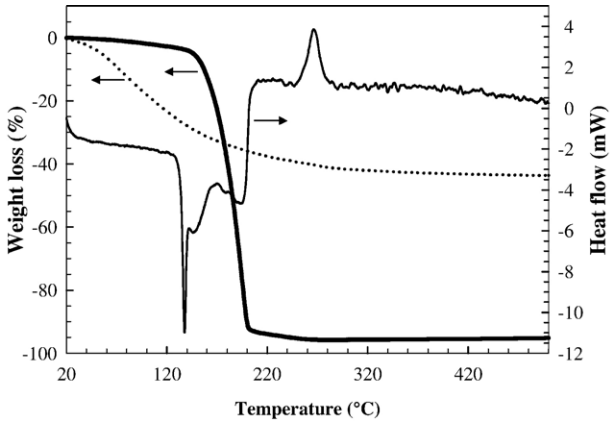

Fig. 4. TGA and DTA curves for a fresh sample of ATI (solid line) and TGA curve for a sample maintained at 110 °C for 15 h (dotted line).

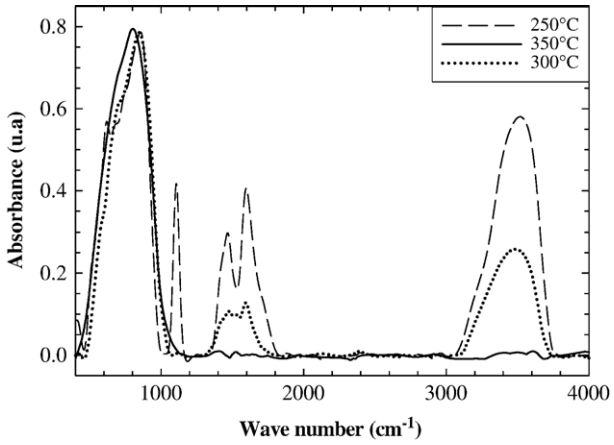

Fig. 5. Transmittance FTIR spectra for films deposited on silicon substrates at various temperatures with water vapour added in the gas phase.

however, this system gives glassy films of reasonable quality with very reproducible growth rates".

2.3. Infrared study

Fig. 3 shows the FTIR spectra for a sample of ATI fresh and after different times of exposure to ambient atmosphere. After 8 days, a wide adsorption band between 2800 and 4000 cm^{-1} and fine lines between 3000 and 3150 cm^{-1} and at 3654 cm^{-1} have appeared. They reveal the formation of variously bonded OH groups resulting from hydrolysis. Fine lines characteristic of the methyl groups are still present between 2800 and 3000 cm^{-1} with respect to the fresh sample. However, the decrease of the fine lines at about 1390 cm^{-1} may be indicative of fading *iso*-propyl groups, thus indicating that *n*-propanol forms instead of *iso*-propanol upon hydrolysis.

The infra-red spectra taken after 2 weeks and after several months are similar. They comprise three wide bands at 600–1250 cm^{-1}, 1250–1800 cm^{-1} and 2600–4000 cm^{-1}, evoking a polymer or a mixture of oxide and hydroxide species.

2.4. Thermal analyses

A fresh sample of ATI (Across, purity 98%) submitted to TG and DT analyses (sample weight: 20.94 mg; N_2 flow: 1.5 l/h; heating rate: 2 °C/min; temperature range: 25–550 °C) showed a sharp weight loss of 90% between 137 °C (melting point) and 200 °C (Fig. 4). About 3% of the initial weight is lost between RT and 137 °C, most likely corresponding to VOC vaporization (mainly propanol). A weight loss of about 2% occurs between 200 and 250 °C, most probably due to the decomposition of a non volatile residue. The total weight loss is 95.2%. Therefore about 90% of the sample did sublime, whereas a tiny amount decomposed on heating. This is in contrast with the only reported TG analysis of ATI by Morssinkhoff [17]. The author did not mention the total weight loss recorded between 200 and 300 °C (heating rate of 10 °C/min), that he attributed to the thermal decomposition of ATI. To confirm the interpretation of our TGA results, two large samples (resp. 262 mg and 342 mg) of ATI were introduced in a Pyrex-glass tube reactor and heated under flowing nitrogen up to 250 °C and 300 °C respectively, in the conditions of the thermal analysis. No traces of decomposition of the vapour phase appeared on the reactor wall in the heated zone. Out flowing ATI vapours condensed on the cold reactor wall as a colourless, transparent, viscous liquid. The residues represented 4.0% (250 °C) and 3.5% (300 °C) of the initial weight.

A sample of ATI was also submitted to TG and DT analyses after being maintained at 110 °C for 15 h. Then the weight loss spread over the whole temperature range of study, and amounted to 43% only. This dramatic change in thermal behaviour confirmed the necessity not to use the same precursor charge more than a few hours for comparative and reproducible CVD experiments. We have noticed that obtaining reproductive deposition rates requires using ATI charges having about the same thermal history.

2.5. MOCVD from ATI

The MOCVD experimental set-up has been described elsewhere [1,4]. The precursor was used as received. It was stored under argon in a metallic glove box. It was used as a supercooled melt at 110 °C, with the carrier gas (N_2) bubbling through. The

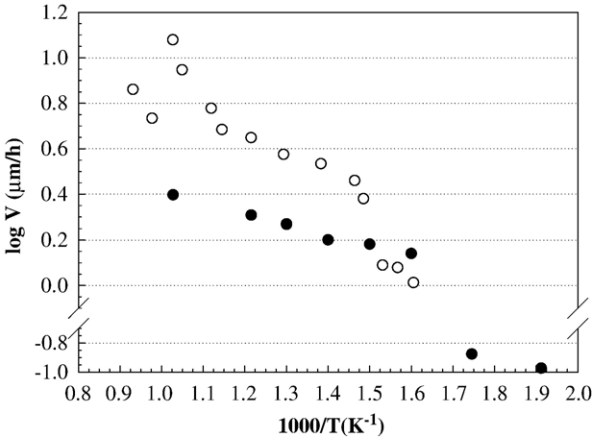

Fig. 6. Growth rate Arrhenius plots for films prepared by pyrolytic decomposition of ATI (open circles) and with water vapour added in the gas phase (black dots).

precursor charge was changed after 10–12 h of use at this temperature. The saturator was always refilled in open atmosphere.

A first series of films (series A) was prepared with ATI vapour and pure N_2 (carrier and dilution gas) as the only components of the gas phase (pyrolytic decomposition). A second series of films (series B) was prepared with adding water vapour in the gas phase. Depositions were performed at low pressure (667 Pa for the first series, 2000 Pa for the second series) in the temperature range 250–700 °C. Water vapour was generated by bubbling dry N_2 in a water container maintained at 1 °C (water vapour pressure = 667 Pa).

The deposits grown in this range of temperature do not diffract X-rays. An electron diffraction study showed that films of the A series were amorphous when prepared at 350 °C and nanocrystalline when prepared at 700 °C.

Varied elemental analyses [electron probe microanalysis (EPMA), energy dispersive X-ray spectroscopy (EDX), elastic recoil detection analysis (ERDA) and Rutherford back-scattering spectroscopy (RBS)], FTIR transmission spectroscopy and thermal gravimetric analysis showed that the films of the A series were composed of Al_2O_3 when deposited above 415 °C. At 350 °C, the formula was very close to AlO(OH). The transition from hydroxyled alumina to Al_2O_3 takes place between 350 and 415 °C, and is rather sharp [3].

FTIR transmission spectroscopy showed that none of the films of the B series prepared at 350 °C and above contained hydroxo species (Fig. 5). EPMA and EDX elemental analysis for this series of films showed the O/Al ratio very close to that of a standard sample of α-Al_2O_3. It is therefore possible to lower the deposition of Al_2O_3 to 350 °C at least by adding water in the gas phase. The films prepared in the same conditions at 300 °C and 250 °C contained hydroxo species as shown by the FTIR spectra (Fig. 5)

Arrhenius plots of growth rate *versus* deposition temperature are presented for the two series of films between 350 and 700 °C on Fig. 6. Growth rates were measured by dividing film thickness by the time of deposition. The plot for films of the A series shows two segments intersecting at about 420 °C. The rates measured below 415 °C correspond to the deposition of partly or totally hydroxylated films, i.e. films whose composition varies with temperature. It is therefore not appropriate to extract activation energy from these measures. Above 415 °C they correspond to the deposition of pure alumina. The activation energy is *ca.* 12 kJ/mole. The plot for the films of the B series shows that the growth rates lessen when water is added in the gas phase. The activation energy is 9 kJ/mole. The weak activation energies lead to propose that the growth is diffusion controlled for the two series of films.

3. Conclusions

Despite its instability and trend to ageing, ATI can be used for depositing aluminium oxide provided that it is stored in a glove box, and renewed in the bubbler after a few hours of use. Interestingly enough, water vapour assisted MOCVD of aluminium oxide from ATI yields amorphous pure alumina at temperature as low as 300–350 °C and above. This temperature is one of the lowest reported in the literature for the processing of pure alumina films and is about 80 °C lower than through thermal decomposition of ATI. Despite the low temperature, it is the ATI concentration in the input gas that controls film growth rate. Potential applications for the use of amorphous alumina as oxidation barrier applied on thermally sensitive materials are currently investigated.

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